

## **EXFOLIATED NANOCCLAYS**

### **FIELD OF THE INVENTION**

The present invention relates to intercalated layered materials. More particularly, the present invention relates to intercalated and exfoliated nanoclays. The present invention also relates to a method for the preparation of exfoliated nanoclays. More particularly, the present invention relates to a method for the preparation of exfoliated nanoclays by contracting and thereby intercalating, a polymer between and within platelets of mineral clay such as bentonite, by adsorption or flow. The resulting clay is filtered, dried and tested by X-ray diffraction. This results in producing exfoliated nanoclays from layered mineral clays.

### **BACKGROUND OF THE INVENTION**

Recent advances in polymer/clay and polymer/silicate nano-composite materials have inspired efforts to disperse montmorillonite-based fillers in PP. Although it has been long known that polymers can be mixed with appropriately modified clay minerals and synthetic clays, the field of polymer/silicate nano-composites has gained large momentum recently. Two major research findings pioneered the revival of nanomaterials: First, the report of a nylon-6/montmorillonite material from Toyota research [Y.; Kurauchi T.T., Kamigaito, O.J Mater. Res. 1993, 8, 1179-1185 and Kojima, Y.; Usuki, A; Kawasumi, M; Okada, A.; Kurauchi, T.T.; Kamigaito. O.J Polym. Sci. Part A: Polym. Chem. 1993, 31 983], where very moderate inorganic loadings resulted in concurrent and remarkable enhancements of thermal and mechanical properties. Second Giannelis et al. [Vaia, R.A.; Ishii, H.; Giannelis, E. P. Chem. Mater, 1993, 5, 1694-1696] found that it is possible to melt-mix polymers with clays without the use of organic solvents. Since then, the high promise for industrial applications has motivated vigorous research, which revealed concurrent dramatic enhancements of many materials properties by the nano-dispersion of inorganic silicate layers. Intercalated and exfoliated structures may coexist in nanocomposites.

The present invention relates to production of nanoclays for creating new markets for polymer nanocomposites from all types of plastics [biopolymers, thermoplastics, engineering plastics, thermosets, fibers, etc.] and boosting per capita consumption of plastic without posing any threat to environment.

Nanoclay is the latest layered clay for making plastics nanocomposites which have superior mechanical properties, barrier properties and flame resistance over conventional plastics and yet their optical properties remain intact because the addition level of nanoclay is in 1 to 6% range. In market the availability of nanoclay is very expensive [\$55/lb] and it is also marketed as masterbatches to mask its identity. This exorbitant cost is an inhibiting factor, which prevents widespread use of nanoclays in plastics and wider use of nanocomposites in many areas.

International companies, such as Polyone, Nanocor, RTP inc., Southern Clay Products inc., etc. are well known suppliers of nanoclys/masterbatches.

The purpose of this invention is to provide unrestricted availability of nanoclays to plastic producers and plastics processors-small as well as large-to create vast, untapped global markets for plastics. A decade ago nanocomposite technology was a concept with great potential. Today, it is a reality. Nanoclays are surface modified montmorillonite minerals available for a range polymer resins from commodity polyolefins to specialty polyamides. Incorporation into these resins forms a nanocomposite plastic. Because Nanoclays are used at low addition levels, significant property improvement is achieved with lighter weight parts. Nanoclays have platey morphology.

#### **DESCRIPTION OF THE PRIOR ART**

The layered clays originated from volcanic ash. Common clays are naturally occurring minerals. The term "Bentonite" was applied for the first time to a particular kind of clay discovered near Fort Benton, Wyoming. This clay displays strong colloidal properties and when in contact with water, increases its volume several fold by swelling, giving rise to a thixotropic, gelatinous substance, but the other clay minerals such as illite and Kaolinite may be present. The composition of montmorillonite [MMT] itself varies from one bentonite to another, but lies in the range of 75-95%.

Layered smectite- type MMT, a hydrous alumina silicate mineral whose lamellae are constructed from octahedral alumina sheets sandwiched between two tetrahedral silicate sheets, exhibits a net negative charge on the lamellar surface, which enables them to adsorb cations, such as  $\text{Na}^+$  or  $\text{Ca}^{++}$ . Compatibility with various polymers is accomplished by modifying the silicates with alkylammonium cations via an ion exchange reaction [[Y.; Kurauchi T.T., Kamigaito, O.J Mater. Res. 1993, 8, 1179-1185 and Kojima, Y.; Usuki, A; Kawasumi, M; Okada, A.; Kurauchi, T.T.; Kamigaito. O.J Polym. Sci. Part

A: Polym. Chem. 1993, 31 983]]. Because the negative charge originates from the silicate layer, the cationic head groups of the alkylammonium molecule preferentially reside at the layer surface, while the aliphatic tail is removed from the surface. The presence of these aliphatic chains in the galleries modifies the original hydrophilic silicate surface to be organophilic. Furthermore, the organic cations contain various functional groups that react with the polymers and reinforce adhesion between the particles and the matrix, thus producing nanocomposites with excellent dispersion quality in organic solvents. As the surfactant chain length gets larger, the charge density of the clay and the spacing between the clay layers increase. When shear is employed for exfoliation, any method which can be used to apply a shear to the intercalant/carrier composition can be used. The shearing action can be provided by any appropriate method, as for example by mechanical means, by thermal shock, by pressure alternation, or by ultrasonics, all known in the art. In particularly useful procedures, the composition is sheared by mechanical methods in which the intercalate, with or without the carrier or solvent, is sheared by use of mechanical means, such as stirrers, Banbury. RTM. Type mixers, long continuous mixers, and extruders.

There have been several innovations in this area and many patents have been granted. AMCOL International Corporation has been active in seeking patent protection in this field and Nanocor is the beneficial holder of over two dozen US patents. US 6,399,690 (2002) granted the above said company describes preparation of layered compositions with multicharged onium ions as exchange cations and their application to prepare intercalated and nanocomposites. US Patent No. 6,391,449 (2002) issued to the same company reveals methods of preparing polymer clay intercalates, exfoliates and nanocomposites having improved gas permeability. US Patent No. 6,287,634 (2001) granted to the same company describes intercalates and exfoliates formed with monomeric ethers and esters and composites formed with polymer matrix. EP 084662 (1998) and WO 93 04118 of the same company describe process for manufacturing intercalates and exfoliates with an intercalant surface modifier selected from the group consisting of a compound having an alkyl radical, a compound containing an aromatic ring and mixtures thereof. US Patent No. 6,380,295 (2002) of Rheox Inc. teaches the preparation of hybrid organoclay that consist of an organic chemical / phyllosilicate clay intercalate that has been ion-exchanged with

quaternary ammonium compounds and further their nanocomposites and also as rheological additives. US Patent No.6,07,988 (2000) granted to Eastman Chemical Company illustrates a method for the manufacture of polyester composite material comprising platelet particles treated with at least one polyalkoxylated ammonium salt. JP  
5 Kokai 9-176461, discloses method of making polyester bottles wherein the polyester contains swellable laminar silicate. WO 97/31057 discloses polymer composites having dispersed therein inorganic materials such as clay, which is separated with an inorganic intercalant. WO 97/31973 discloses producing a composite material by mixing potassium ionomer in which an ethylene methacrylate copolymer is either partially or completely  
10 neutralized with an organic polymer. US Patent Nos. 4,739,007 and 5,164,460 disclose polyamide and polyimide composite materials respectively containing layered clay mineral intercalated with organic salts.

In all the above patents, the intercalant were organic solvents. The organic pretreatment of the clay adds to the cost of the clay, even though the clay are relatively  
15 cheap. Need for intercalated and exfoliated clays has been growing as the field of Nanocomposites is at an embryonic stage of development today. The present invention is carried out to fulfill the requirement for a cost effective intercalated [more preferably] bentonite clay and its nanocomposites there of with at least one polyolefine polymer such as polypropylene. The composites disclosed in this invention can be used for a myriad  
20 number of applications to biopolymers, thermosets, also such as furniture, automobile components, body parts, and parts left to the imagination of the moulder.

Further, as described in Greenland, Adsorption of Polyvinyl Alcohols by Montmorillonite, Journal of Colloid Sciences, Vol 18, page 647-664 (1963), polyvinyl alcohols containing 12% residual acetyl groups could increase the basal spacing by only  
25 about 10. Å. Due to the sorbed polyvinyl alcohol (PVA). As the concentration of polymer in the intercalant polymer-containing solution was increased from 0.25% to 4% the amount of polymer sorbed was substantially reduced, indicating that sorption might only be effective at polymer concentrations in the intercalant polymer-containing composition on the order of 1% by weight polymer, or less.

30 Exemplary prior art composites, also called "nanocomposites", are disclosed in published PCT disclosure of Allied Signal, Inc. WO 93/04118 and U.S. PatENT. No.

5,385,776, disclosing the admixture of individual platelet particles derived from intercalated layered silicate materials, with a polymer to form a polymer matrix having one or more properties of the matrix polymer improved by the addition of the exfoliated intercalate. As disclosed in WO 93/04118, the intercalate is formed (the interlayer spacing between adjacent silicate platelets is increased) by adsorption of a silane coupling agent or an onium cation, such as a quaternary ammonium compound, having a reactive group which is compatible with the matrix polymer. A publication that discloses direct intercalation (without solvent) of polystyrene and Poly (ethylene oxide) in organically modified silicates is Synthesis and properties of Two dimensional Nanostructures by Direct Intercalation of Polymer Melts in Layered Silicates, Richard A. Vaia, et al. Chem. Mater., 5: 1694-1696 (1993). Also as disclosed in Adv. Materials, 7 No. 2: (1985), pp, 154-156, New Polymer Electrolyte Nanocomposites: Melt Intercalation of Poly (Ethylene Oxide) in Mica Type Silicates, Richard A. Vaia, et al., poly (ethylene oxide) can be intercalated directly into Namontmorillonite and Li-montmorillonite by heating to 80°C. for 2-6 hours to achieve a d-spacing of 17.7 ANG. The intercalation is accompanied by displacing water molecules, disposed between the clay platelets, with polymer molecules.

#### DEFINITIONS

Whenever used in this Specification, the terms set forth shall have the following meanings:

Phyllosilicate: A layered material

Intercalation: Penetration of any chemical, monomer or polymer in between adjacent layers of clay. "Intercalation" shall mean a process for forming an Intercalate

Exfoliation: Separation of clay layers resulting in their random dispersion. "Exfoliation" shall mean a process for forming an Exfoliate from an Intercalate. "Exfoliate" or

"Exfoliated": Individual platelets of an intercalated Layered Material so that the adjacent platelets of the Intercalated Layered Material can be dispersed individually throughout a carrier material, such as a matrix polymer.

"Intercalant Polymer" or "Intercalant": An oligomer or polymer that is sorbed between Platelets of the Layered Material to form an Intercalant.

Bentonite: A rock name given to the clay ore, which consists of smectite clay impurities such as gravel, shale and limestone

Smetite: A mineral clay that has been the ability to swell in water. The most commercially important forms are hectorite and montmorillonite. The small particle sizes and melt dispersion potential of nanoclays allow thin sections to maintain clarity with filler loadings as high as 5%

- 5 Montmorillonite: The most available form of clay, classified as a magnesium silicate having a dioctahedral structure and a platy or sheet like morphology.

Cation: A positively charged ion.

Gallery: The spacing between parallel layers of montmorillonite clay platelets. The spacing changes depending upon which polymer or surface treatment occupies the space.

- 10 Intercalant: An organic or semiorganic chemical capable of entering the smectite clay gallery and bonding to the surface.

Intercalate: Treated clay that has a complex formed between the clay surface and an organic molecule. "Intercalate" or "Intercalated" shall mean a Layered Material that includes oligomer and/or polymer molecules disposed between adjacent platelets of the

- 15 Layered Material to increase the interlayer spacing between the adjacent platelets to at least 10 Angstroms.

Interlayer spacing: Also known as the gallery.

- Layered Material: An inorganic material, such as a smectite clay, mineral, that is in the form of a plurality of adjacent, bound layers and has a maximum thickness, for each layer,  
20 of about 100 Angstroms.

Platelets: Individual layers of the Layered Material

"Matrix Polymer": A thermoplastic or thermosetting polymer in which the Exfoliate is dispersed to form a Nanocomposite.

- Nanocomposites: A new class of plastics derived from the incorporation of nanoscale  
25 particles into polymers.

"Nanocomposite": An oligomer, polymer or copolymer having dispersed therein a plurality of individual platelets obtained from an Exfoliated, Intercalated Layered Material.

- X-Ray Diffraction (XRD): It is also known as wide-angle- x ray scattering. It is one of the fundamental techniques of Materials Science. It gives a plot of scattered x-ray intensity as  
30 a function of scattering angle [two-theta]. XRD is used to determine crystal structure, crystallinity, crystal/amorphous ratio in polymers, metals, catalysts, adsorbents, etc.

## OBJECTS OF THE INVENTION

It is an object of this invention to provide a process for the preparation of intercalated, preferably, exfoliated clay or more preferably, exfoliated bentonite clay of local origin for preparation of nanocomposites that is economical.

5 It is another object of this invention to provide a process for the preparation of intercalated, preferably exfoliated clay or more preferably exfoliated bentonite clay using an intercalant or an exfoliating agent that is environment friendly in order to prepare bentonite clay.

10 It is another object of this invention to provide a process for the preparation of intercalated, preferably exfoliated clay or more preferably exfoliated bentonite clay that can be used for preparing nanocomposites.

It is another object of this invention to prepare intercalated, preferably exfoliated clay or more preferably exfoliated bentonite clay and use it to prepare nanocomposite with at least one polymer using the method of melt blending.

15 It is yet another object of this invention to use intercalated or exfoliated clay, preferably, bentonite clay alongwith or without a proper compatibilizer or an interfacial agent and melt mix with a polyolefin polymer to prepare a nanocomposite.

## SUMMARY OF THE INVENTION

20 In accordance with one embodiment of the present invention, intercalates are prepared by contacting a phyllosilicate with a organic compound having an electrostatic functionality selected from the group consisting of a hydroxyl; a polyhydroxyl; an aromatic functionality; and mixtures thereof.

Any swellable layered material that sufficiently sorbs the intercalant monomer to increase the interlayer spacing between adjacent phyllosilicate platelets to at least about 5. Å, preferably to at least about 10. Å. (when the phyllosilicate is measured dry) may be used in the practice of this invention. Useful swellable layered materials include phyllosilicates, such as smectite clay minerals, e.g., Montmorillonite, particularly sodium montmorillonite; mangsium montmorillonite and/or calcium montmorillonite; nontronite; beidellite; volkonskoite; hectorite; saponite; sauconite; sobockite; stevensite; svinfordite; 25 vermiculite; and the like. Other useful layered materials include micaceous minerals, such as illite and mixed layered illite/smectite minerals, such as rectorite, tarosovite, ledikite and 30

admixtures of illites with the clay minerals named above. Minerals such as montmorillonite, nontronite, beidellite, volkonskoite, hectorite, saponite, sauconite, sobockite, stevensite, and svinfordite.

Smectite clays contain absorbed molecular water ( $H_2O$ ), which is loosely held.  
5 Therefore, the hydrolysis process which occurs during weathering involves two kinds of hydrogen, bound as either as OH or  $H_2O$ , which is found in two different types of crystallographic site. Under laboratory or factory conditions the crystalline water is lost at higher temperatures than the absorbed interlayer water.

The present method makes use of water-friendly nature of clay and not its ion-exchange ability. A neutral hydrophilic molecule enters the gallery of clay and lies flat.  
10 This process is repeated until the gallery expands and "exfoliation" occurs. Water molecules of clay are absorbed by intercalant, thus breaking crystal lattice of clay partially or totally. Another method to convert clay into nanoclay is by variations of freeze-drying technique which eliminates water molecules from various locations in clay-the crystallites,  
15 intralayer water, water absorbed on surface of platelets etc. In accordance with an important feature of the present invention, best results are achieved using the organic compound, having at least one of the above-defined functionalities, in a concentration of at least about 2% preferably at least about 5% by weight functional organic compound, more preferably about 30% to about 80% by weight, based on the weight of functional organic  
20 compound and carrier (e.g., water, with or without an organic solvent for the functional chemical compound) to achieve better sorption of the functional monomeric organic compound between phyllosilicate platelets.

#### DETAILED DESCRIPTION

The present invention will now be described in greater detail with reference to the  
25 accompanying drawings wherein:

Figure 1: A comparison of the x-ray diffractograms of bentonite and nanoclay made by, modifying it [BIO-CLAY]; and

Figure 2: shows a schematic representation of the process of the present invention.

Smectite clays can be intercalated sufficiently for subsequent exfoliation by  
30 sorption of polymers having carbonyl, carboxyl, hydroxyl amide, amine, phosphate or aromatic rings to provide complexing or bonding of the intercalant [chemical activator] to



the inner platelet surfaces of the clay. Water compatible or soluble or slurry forming polymers are chosen as intercalants for making nanoclay from layered silicate materials (clays). These can provide the necessary hydrogen bridge bonds between the hydroxyl groups of the platelets. Addition of polar substance attains delamination ["exfoliation"] by penetrating between the platelets forcing them apart by internal pressure. Application of shear forces may sometimes be necessary to achieve a complete exfoliation of clay into so-called nanoclay.

In the present work, clay is interacted with an aqueous solution or suspension of a natural or modified polysachharide till its penetration and absorption reaches saturation. The carbohydrate penetrates between the platelets, forcing them apart. Application of shear completes the dispersion of nanoclay. The intercalation or exfoliation of treated clay is judged by the presence or absence of peaks in X-ray diffraction pattern or diffractogram. Intercalated clay is not a nanoclay but is a precursor of it. When an intercalated clay is subjected to high shear in a twin -screw extruder, it gets exfoliated to different extents subject to degrees of applied shear. Exfoliated clay is the true nanoclay as it shows an amorphous, non-crystalline structure and does not probably need shear to disperse individual clay layers or platelets. In the X-ray diagrams, exfoliated clay shows a complete lack of diffraction peaks or a residual small, broad peak. Figure 1 is an example of XRD of exfoliated nanoclay produced by an intercalation of carbohydrate molecule. Usually, intercalated structures that are characterized by parallel registry give rise to X-ray peak at d-spacings in the range 20-30A.

In a specific embodiment of the present invention, as shown in Figure 2, Bentonite is converted into exfoliated nanoclay by an ingenious scheme under which a mixture of various carbohydrate molecules slip layer-by-layer into the interlayer gallery. Once there, these molecules physically block bonding between adjacent clay layers thus preventing a recrystallization of clay ["exfoliation"]. Layers get dismantled.

Carbohydrate intercalants may be of natural origin or may have been synthetically modified. Further, they may have a linear structure or may be branched. Their molecular weight may lie anywhere between 400-200,000.

Carbohydrates may be of plant or seaweed origin, e.g., potato, maize, rice or may belong to following molecular species: aligins, okra, industrial gum, pectins, mannans,

amylopectins, amylosearabinoxylans, carrageenans, gum arabic, cellulose, chitin, xanthan, galactoglucomannans, glycogens, polydextrose, agars, guar gum, cationic starches, wheat starch, tapioca starch, chitosans, oxidized starches, starch acetates/phosphates/succinates, etc.

5        Taking starch as an example, the viscosity obtained by cooking a suspension of starch is determined by the starch type, derivatization and/or modification, solids concentration, pH, amount of agitation during heating, rate of heating, maximum temperature reached, time held at that temperature, agitation during holding and presence of other ingredients. An aqueous dispersion of an unmodified starch containing amylose  
10 will gradually form an insoluble precipitate through association of linear segments.

Bentonite clay is kept soaked in a [0-20%] solution or suspension of chosen carbohydrates in aqueous alcohol with alcohol content in the range 0-15% for a period 5-25 hours. The clay thus modified is dried at the end of experiment to give an -ray silent spectrum of exfoliated nanoclay.

15        In accordance with the present invention, it has been found that a phyllosilicate, such as a smectite clay, can be intercalated sufficiently for subsequent exfoliation by sorption of organic compounds that have a hydroxyl or polyhydroxyl functionality; or at least one aromatic ring to provide bonding between two functional hydroxyl groups of one or two intercalant monomer molecules and the metal cations of the inner surfaces of the  
20 phyllosilicate platelets. Sorption or bonding of a platelet metal cation between two hydroxyl groups of the intercalant organic molecules; or the bonding between the interlayer cations in hexagonal or pseudo-hexagonal rings of the smectite platelet layers and an intercalant monomer aromatic ring structure, is provided by a mechanism selected from the group consisting of ionic complexing; electrostatic complexing; chelation; hydrogen  
25 bonding; dipole/dipole; Van Der Waals forces; and any combination thereof. Such intercalated phyllosilicates can be easily exfoliated into individual phyllosilicate platelets before or during admixture with a liquid carrier, aqueous solution or solvent, for example, one or more monohydric alcohols, such as methanol, ethanol, propanol, and/or butanol; polyhydric alcohols, such as glycerols and glycols, e.g., ethylene glycol, propylene glycol,  
30 butylenes glycol, glycerine and mixtures thereof; aldehydes ketones; carboxylic acids; amines; amides; and other organic solvents.

In accordance with another embodiment of the present invention, the intercalates can be exfoliated and dispersed into one or more melt processible thermoplastic and/or thermosetting matrix oligomers or polymers, or mixtures thereof. Matrix polymers for use in this embodiment of the process of this invention may vary widely, the only requirement is that they are melt processible. In this embodiment of the invention, the polymer includes at least ten (10), preferably, at least thirty (30) recurring monomeric units. The upper limit to the number of recurring monomer units is not critical, provided that the melt index of the matrix polymer under use conditions is such that the matrix polymer forms a flowable mixture. Most preferably, the matrix polymer includes from at least about 10 to about 100 recurring monomeric units. In the most preferred embodiments of this invention, the number of recurring units is such that the matrix polymer has a melt index of from about 0.01 to about 12 grams per 10 minutes at the processing temperature.

Thermoplastic resins and rubbers for use as matrix polymers in the practice of this invention may vary widely. Illustrative of useful thermoplastic resins, which may be used alone or in admixture, are polyactones such a poly (pivalolactone), poly (caprolactone) and the like; polyurethanes derived from reaction of diisocyanates such as 1,5- naphthalene diisocyanate; p-phenylene diisocyanate, m-phenylene diisocyanate, 2,4-toluene diisocyanate, 4,4'-diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl 4,4' biphenyl diisocyanate, 4,4'- diphenylisopropylidene diisocyanate, 3,3'-dimethyl- 4'4'- diphenyl diisocyanate, 3,3,- dimethyl-4,4'- diphenylmethane diisocyanate, 3,3'-dimethoxy- 4,4'- biphenyl diisocyanate, dianisidine diisocyanate, toluidine diisocyanate, hexamethylene diisocyanate, 4,4'-diisocyanatodiphenylmethane and the like and linear long -chain diols such as poly (tetramethylene adipate), poly (ethylene adipate), poly (1,4-butylene adipate), poly (ethylene succinate), poly (2,3- butylenes succinate), polyether diols and the like; polycarbonates such as poly>methane bis (4-phenyl) carbonate!, poly<1,1- ether bis (4-phenyl) carbonate, poly> diphenylmethane bis (4-phenyl) carbonate!, poly> 1, 1- cyclohexan bis (4-phenyl) carbonate and the like; polysulfones; polyethers; polyketones; polyamides such as poly (4-amino butyric acid), poly (hexamethylene adipamide), poly (6- aminohexanoic acid), poly (m-xylene adipamide), poly (p-xylilen sebacamide), poly (2,2,2-trimethyl hexamethylene terephthalamide), poly (methaenylene isophthalamide) NOMEX), poly (p-phenylene terephthalamide)

(KEVLAR), and the like; polyesters such as poly (ethylene azelate), poly (ethylene- 1,5-naphthalate, poly (1,4-cyclohexane dimethylene terephthalate), poly (ethylene oxybenzoate) (A-TELL), poly (Para-hydroxy benzoate (EKONOL), poly (1,4-cyclohexylidene dimethylene terephthalate) KODEL (as), poly (1,4-cyclohexylidene dimethylen  
5 terephthalate (Kodel( (trans), polyethylene terephthalate, polybutylene terephthalate and the like; poly (arylene oxides such poly (2,6-dimethyl- 1,4-phenylene oxide), poly (2,6-diphenyl - 1,4-phenylene oxide) and the like; poly (arylene sulfides) such poly (phenylene sulfide) and the like; polyetherimides, vinyl polymers and their copolymers such as polyvinyl acetate, polyvinyl alcohol, polyvinyl chloride; polyvinyl and the like;  
10 polyacrylics, polyacrylate and their copolymers such as polyethyl acrylate, poly (n-butyl acrylate), polymethylmethacrylate polyethyl methacrylate, poly (n-butyl methacrylate), poly (n-propyl methacrylate), polyacrylamide, polyacrylonitrile, polyacrylic acid, ethylene-acrylic acid copolymers, ethylene-vinyl alcohol copolymers acrylonitrile copolymers, methyl methacrylate-styrene copolymers, ethylene-ethyl acrylate copolymers,  
15 methacrylated butadiene -styrene copolymers and the like; polyolefins such as low density poly (ethylene), poly (ethylene), poly (Propylene), chlorinated low density poly (4-methyl-1- pentene), poly (ethylene) poly (styrene), and the like; ionomers; poly (epichlorohydrins); poly (urethane) such as the polymerization product of diols such as glycerin, trimethylol-propane, 1,2,6-hexanetriol, sorbitol, pentaerythritol, polyether  
20 polyols, polyester polyols and the like with a polyisocyanate such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4' diphenylmethane diisocyanate 1,6-hexamethylenediisocyanate, 4,4'- dicyclohexylmethane diisocyanate and the like; and polysulfones such as the reaction product of the sodium salt of 2,2-bis (4-hydroxyphenyl) propane and 4,4'- dichlorodiphenyl sulfone; furan resins such as poly (furan); cellulose  
25 ester plastics such as cellulose acetate, cellulose acetate butyrate, cellulose propionate and the like; silicones such as poly (dimethyl siloxane), poly (dimethyl siloxane), poly(dimethyl siloxane co- phenylmethyl siloxane), and the like; protein plastics; and blends of two or more of the foregoing .

The present invention will now be described with reference to the following  
30 illustrative but nonlimiting Examples:

**Example 1 to 3:**

## **Method of Preparation of Nanoclay**

### **Example 1**

10 gm rice was boiled in 1 litre of water. It was cooled and its solids concentration was measured and subsequently adjusted to 1%. About 25 gm of sodium bentonite clay, having a moisture of 20%, was kept in a 1-litre beaker and a 250 ml of rice solution-cum-slurry was added to it. Another 250 ml of de-ionized water was added to beaker containing clay mass. The system was kept undisturbed for 2 days, after which it was dewatered by filtration and oven-dried at 90 °C, until it reached constant weight. Nanoclay was ground to pass through 100-mesh sieve. Its x-ray diffractogram was taken to establish its exfoliation.

### **Example 2**

0.1% aqueous glycerol solution, 125 ml was added to about 25 gm of sodium bentonite clay, having a moisture of 20%. Then it was stirred well to make mass homogeneous. The system was kept undisturbed for 1-2 days, after which it was dewatered by filtration and oven-dried at 90 °C, until it reached constant weight. Nanoclay was ground to pass through 100-mesh sieve. Its x-ray diffractogram was taken to establish its exfoliation.

### **Example 3**

2% aqueous poly(vinyl alcohol) solution, 175 ml was added to about 25 gm of sodium bentonite clay having a moisture of 20%. Then it was stirred well to make mass homogeneous. The system was kept undisturbed for 1-2 days, after which it was dewatered by filtration and oven-dried at 90 °C, until it reached constant weight. Nanoclay was ground to pass through 100-mesh sieve. Its x-ray diffractogram was taken to establish its exfoliation.

### **Example 4**

#### **Preparation and Test Results of PP nanocomposites**

6% of above clays and a commercial clay (Cloisite 20 A) were compounded in our company's 100 gm of polypropylene homopolymer powder having a MFI of 12, with 5% addition of MA-g-PP or a organo-silane. These were dry-mixed for 15 min at ambient temperature. The mixture was premixed for 3 min molded in DSM microcompounder and injection molder for 1 min. Mechanical property testing data for nanocomposites is given in table below :

	Notched Izod Impact Strength [kg-cm/cm]	Tensile Strength at Break [kg/cm <sup>2</sup> ]
Indigenous Nanoclay [Bio-clay]	2.28	291
Commercial Nanoclay [Cloisite 20A]	2.82	81.86

In a conservative estimate, tensile strength at break of indigenous nanoclay nanocomposite is 350% higher than that made from CLOISITE 20A, although at about 20% reduction in impact strength.

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